INCAR Research on Coal Derivatives

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CSIC

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Presentation content

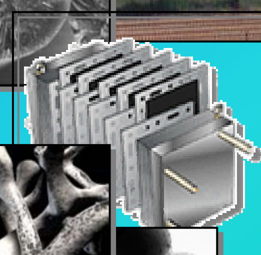
- The National Institute of Coal (INCAR)
- INCAR research on pitch
  - Pitch generalities
  - Pitch modification
    - Thermal treatment
    - Mesophase separation
    - Oxidative treatment
  - New tendencies
    - Hybrid pitch
    - Anthracene oil-based pitch
  - Concluding remarks

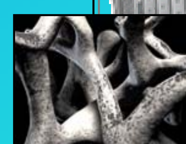
INCAR-CSIC

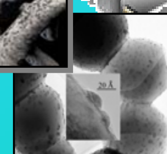

INSTITUTO NACIONAL DEL CARBÓN
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

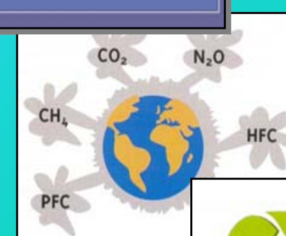

Frecuencia (%)
Rr=0.94%
Rr=1.50%
Contaminantes peligros del aire
Clean Air Act Amendments (CAAA) de 1990
HAPs (Hazardous Air Pollutants)
As Be Cd Co Cr Hg
Mn Ni Pb Sb Se


lignito
bituminoso
antracita
Carbonizado en función del rango



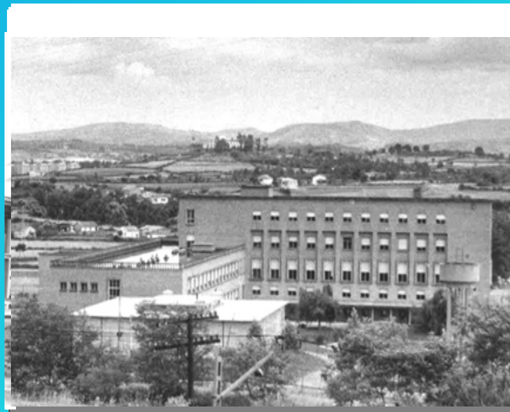




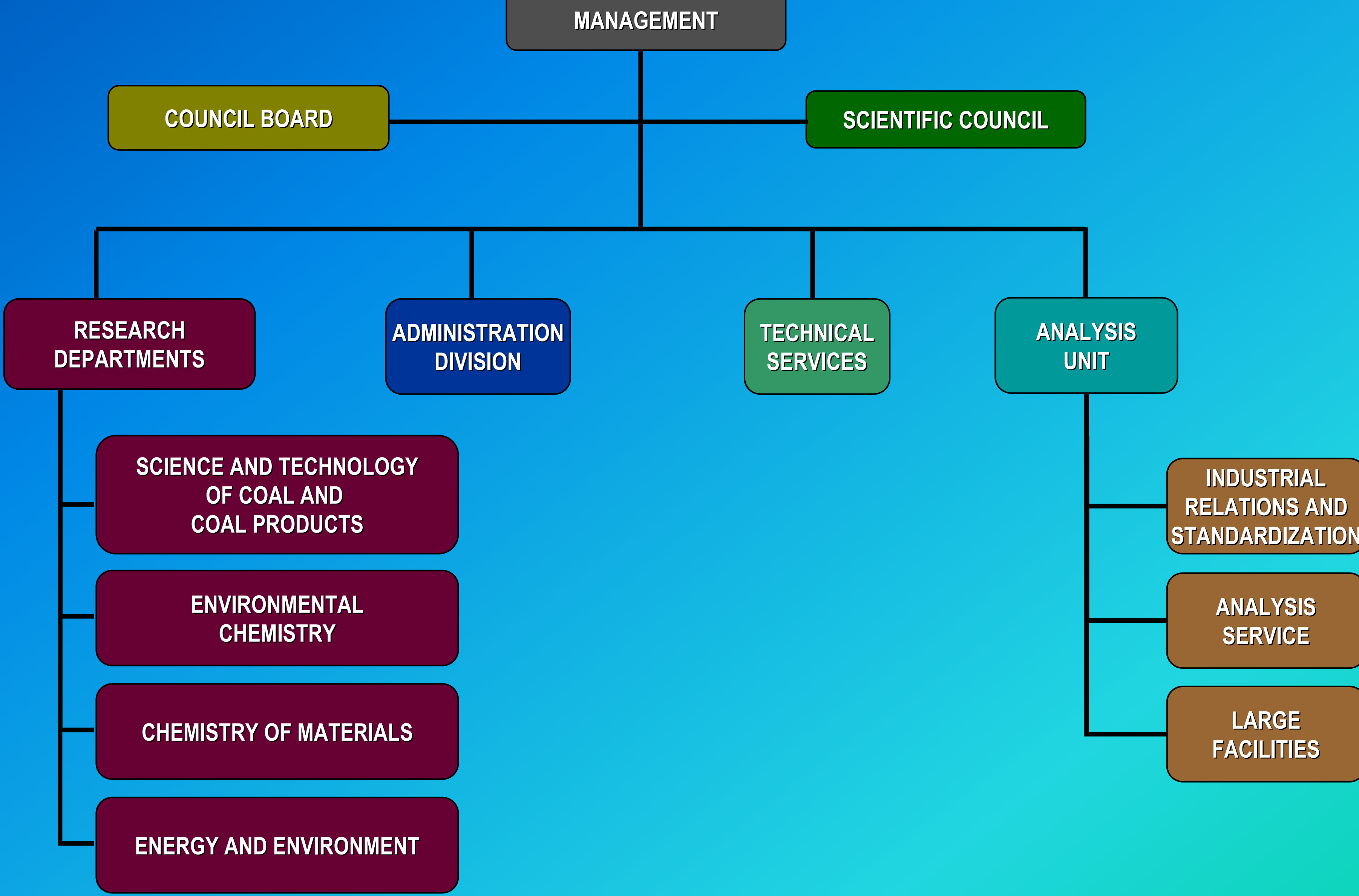

CO2
N2O
CH4
HFC
PFC

Presentation

- CSIC area: Chemistry and Chemical Technology
  - Headquarters in Oviedo (Asturias)



- Founded in 1947 to assist the local mining and steel industry


MANAGEMENT
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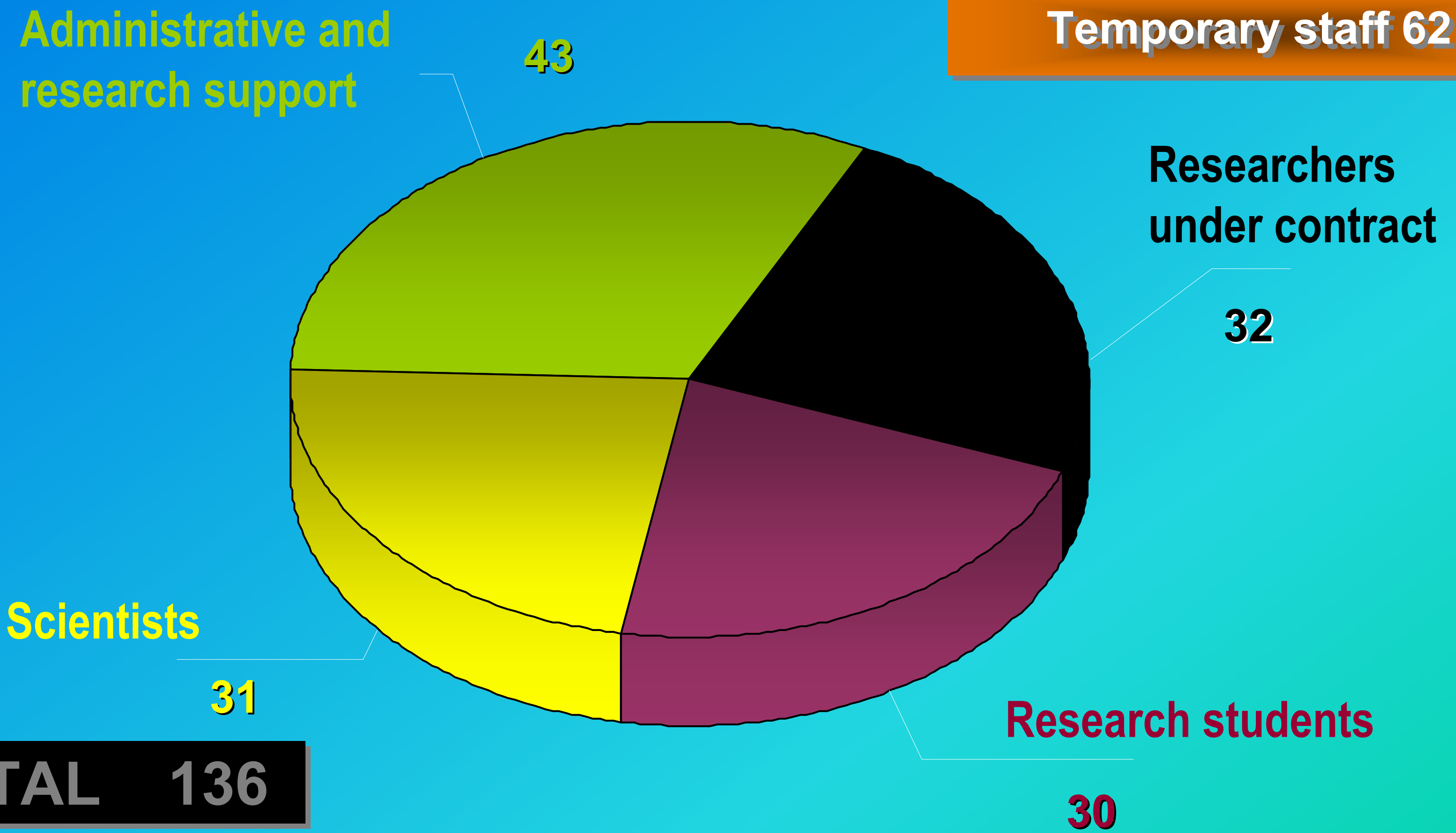
ANALYSIS UNIT
SCIENCE AND TECHNOLOGY OF COAL AND COAL PRODUCTS
ENVIRONMENTAL CHEMISTRY
CHEMISTRY OF MATERIALS
ENERGY AND ENVIRONMENT
INDUSTRIAL RELATIONS AND STANDARDIZATION
ANALYSIS SERVICE
LARGE FACILITIES

Instituto Nacional del Carbón

Consejo Superior de Investigaciones Científicas

Permanent staff 74

Temporary staff 62



TOTAL 136

Coal Conversion

- the optimisation of the coking process for the metallurgical coke production.
- the upgrading of precursors of carbon materials with the aim of improving the competitivity of these materials, reducing their environmental impact and developing new coal-derived products.
- the pollution caused by the utilisation of coal (evaluation and reduction).
- the feasibility of the carbonisation process as an alternative way of recycling industrial residues and plastic residues from the consumer sectors.
- the chemistry of ionic liquids and their application to reactions of PAHs and the treatment of pitch precursors for the preparation of carbon materials.

Research Topics

Energy and Environment

Optimisation of energy resources related with the utilisation of coal and the reduction of pollutants.

- **optimisation of coal blends for hydrogen generation.**
- **mechanisms of formation and reduction of NOx.**
- **design and preparation of adsorbents for the purification of gases and liquids.**
- **CO_2 capture in energy processes based on high temperature treatment (carbonation/calcination).**
- **CO_2 capture in combustion and gasification at moderate temperatures, based on the development of low-cost adsorbents with specific functionalities for the preferential adsorption of CO_2.**

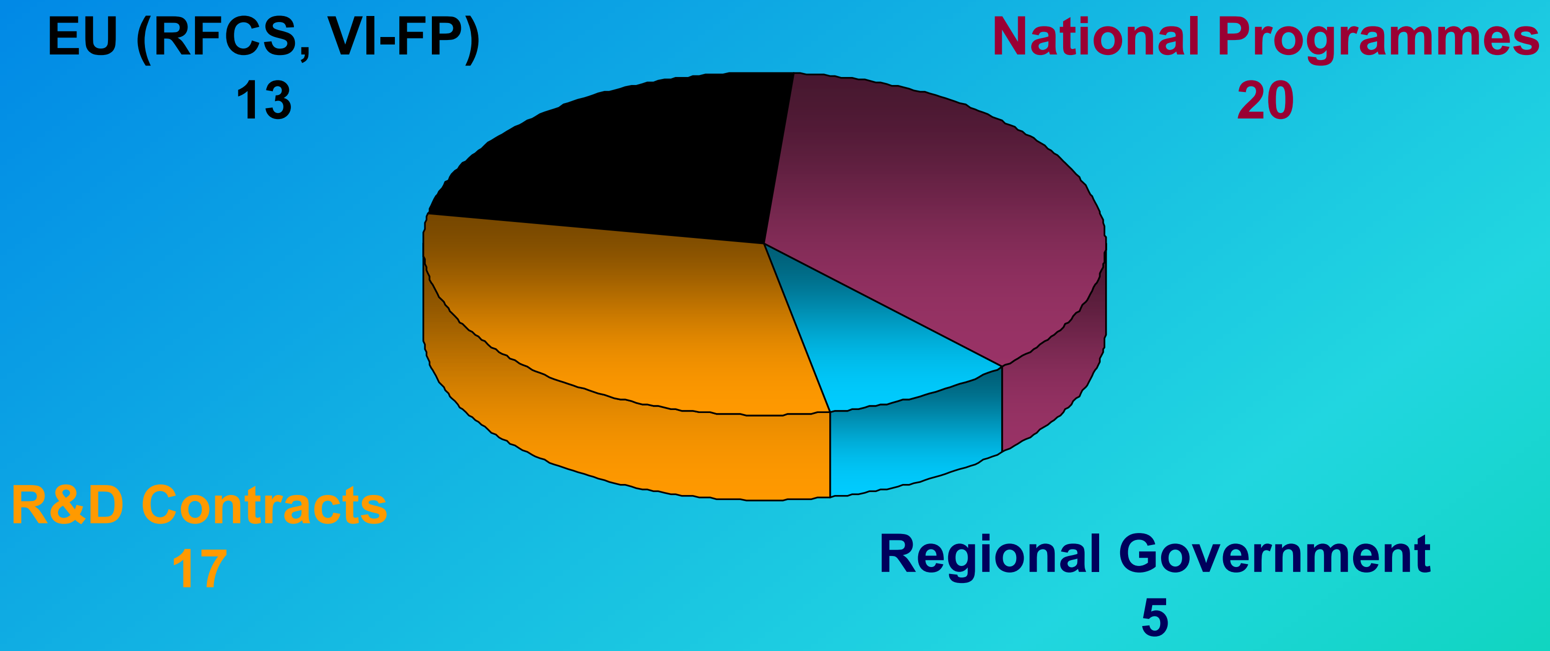
Research Topics

Chemistry of Materials

- Functionalisation of nanostrutured materials.
- Preparation of carbon fibres, polygranular synthetic graphites, special cokes and carbon foams from different coal derivatives.
- Development of C/C composites for extreme conditions (aeronautic and nuclear fusion).
- Carbon materials for the production and storage of energy (batteries and supercapacitors).
- Preparation, characterisation and applications of porous materials.
- Colloidal synthesis of ceramic-ceramic and ceramic-metal nanocomposites for biomedical and microelectronic applications.

55 R&D Competitive Projects (2006)

Regional, national and European Programmes



External Relations

National and Foreign Industries, Universities and Research Centers

Bilateral Actions
Exchange of researchers
R&D Projects
R&D Contracts

INCAR Research on Pitches

INCAR Research Topics on Pitches

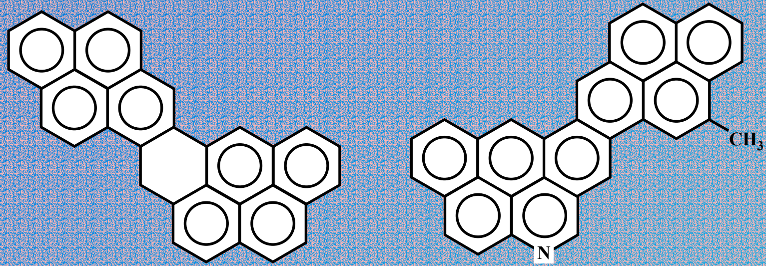
•Composition, structure, pyrolysis behaviour of pitches with a view to understand their transformation into a carbon material and material performance.

•Specific carbon precursors with improved properties from commercial pitches for advanced carbon materials.

•Feasibility of new pitches as potential binder and impregnant for industrial purposes (e.g., carbon anodes and graphite electrodes)

COAL-TAR PITCH

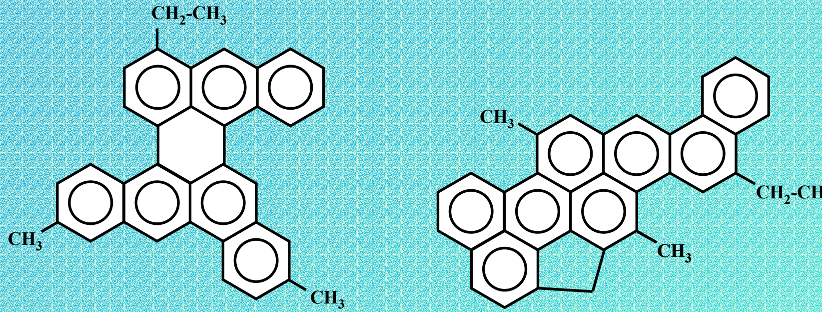
1 in 4 molecules has a CH_2-CH_3 group



Kershaw J.R. & Black K.J.T. Energy & Fuels 1993; 7: 420-425.

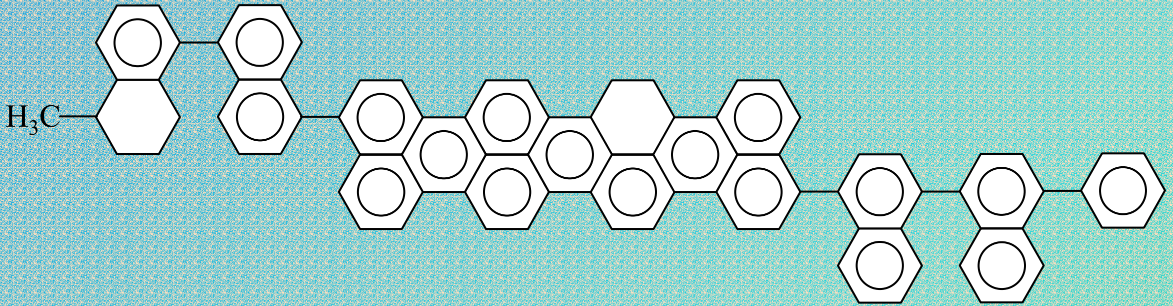
PETROLEUM PITCH

1 in 4 molecules contains S atom



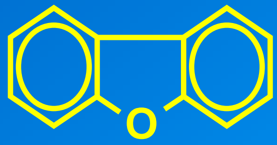
Kershaw J.R. & Black K.J.T. Energy & Fuels 1993; 7: 420-425.

AR-NAPHTHALENE-BASED PITCH

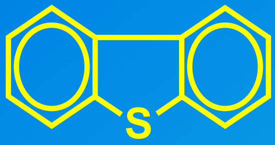


Mitsubischi Gas Chemical Company, Inc.

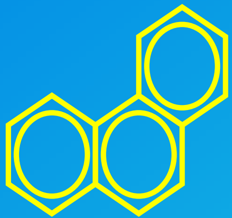
Coal-tar pitch composition



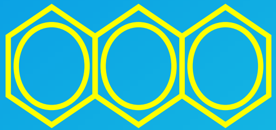
Dibenzofuran



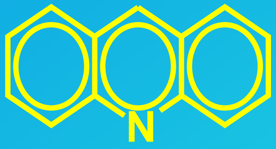
Dibenzothiophene



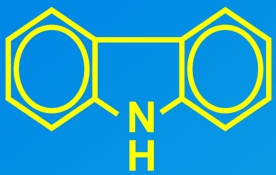
Phenanthrene



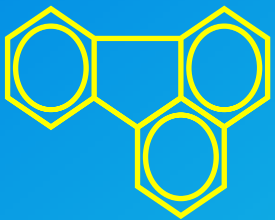
Anthracene



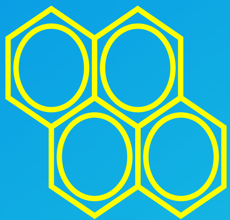
Acridine



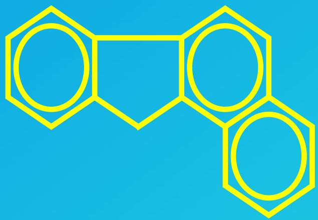
Carbazole



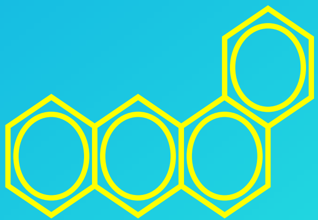
Fluoranthene



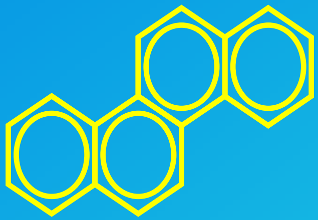
Pyrene



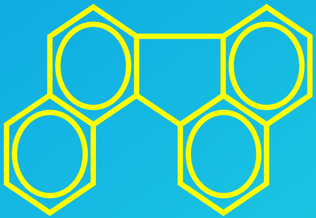
Benzo[a]fluorene



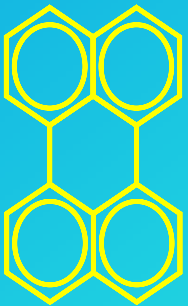
Benzo[a]anthracene



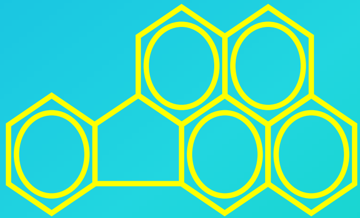
Chrysene



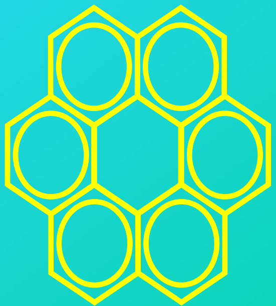
Benzo[j]fluoranthene



Perylene

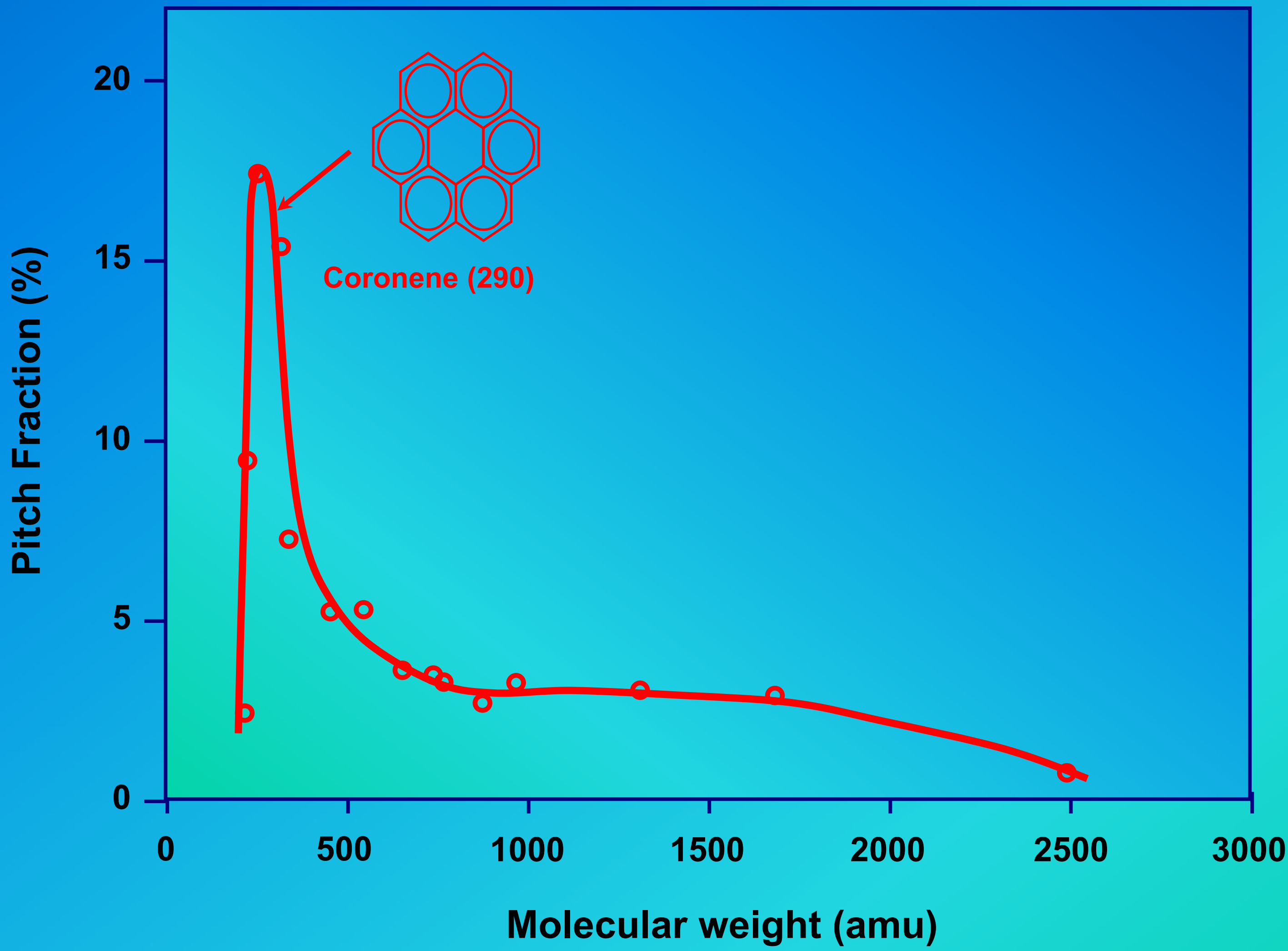


Indeno[1,2,3-cd]pyrene

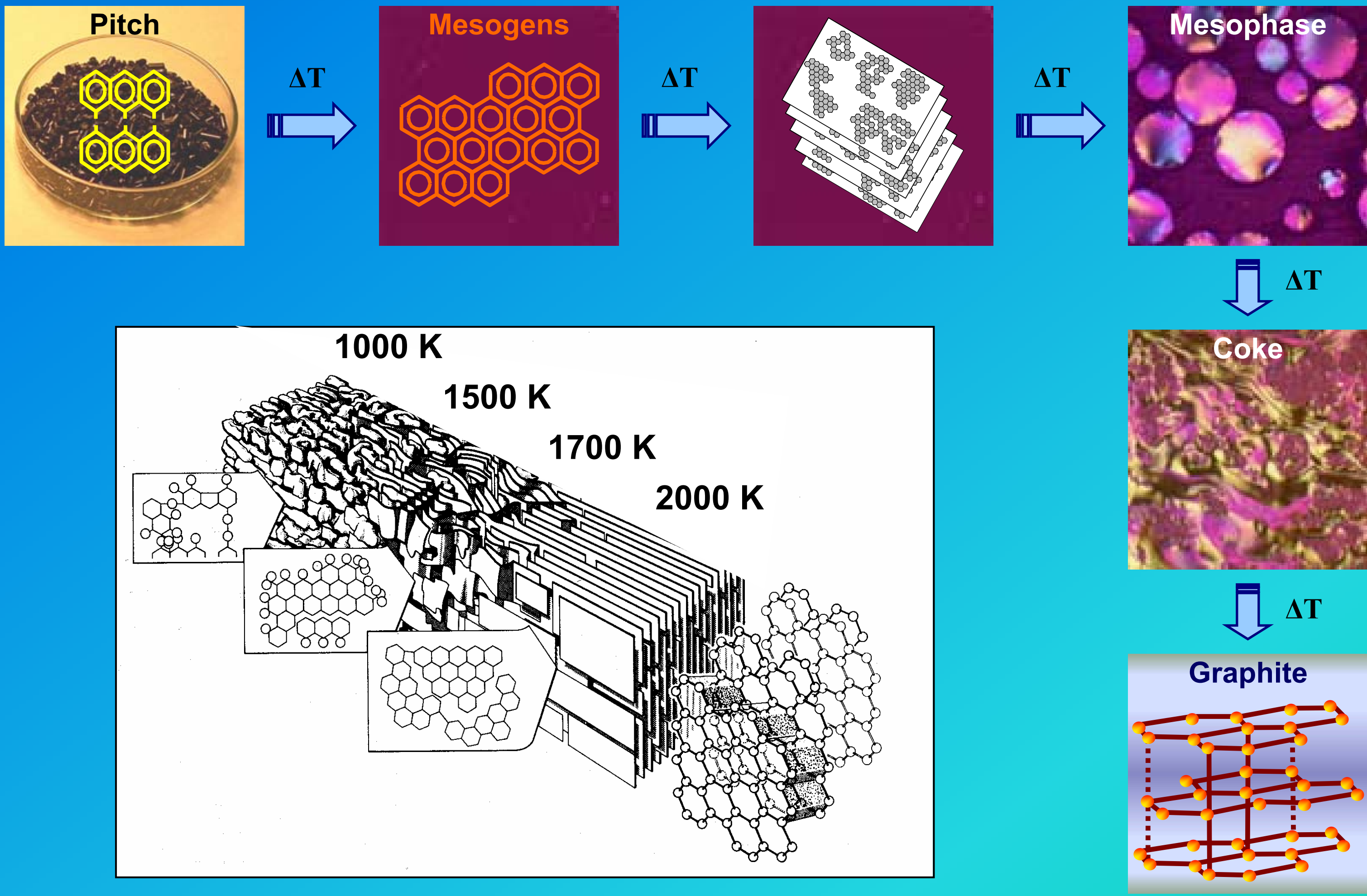


Coronene

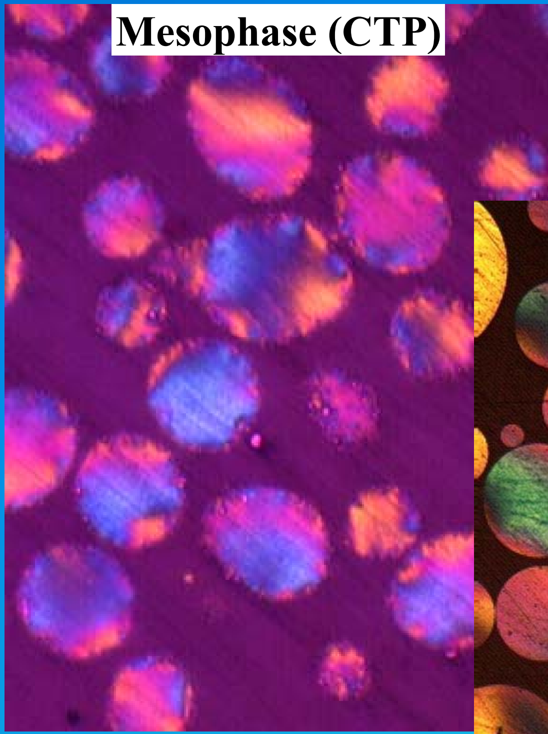
Coal-tar pitch composition - II

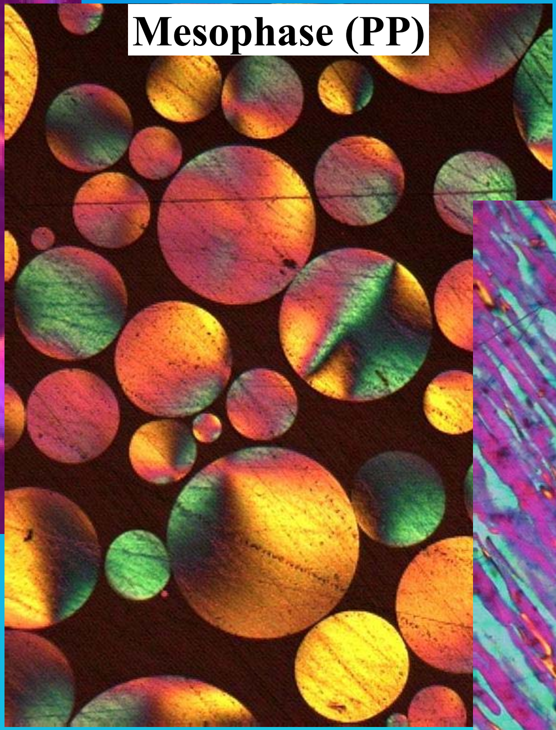


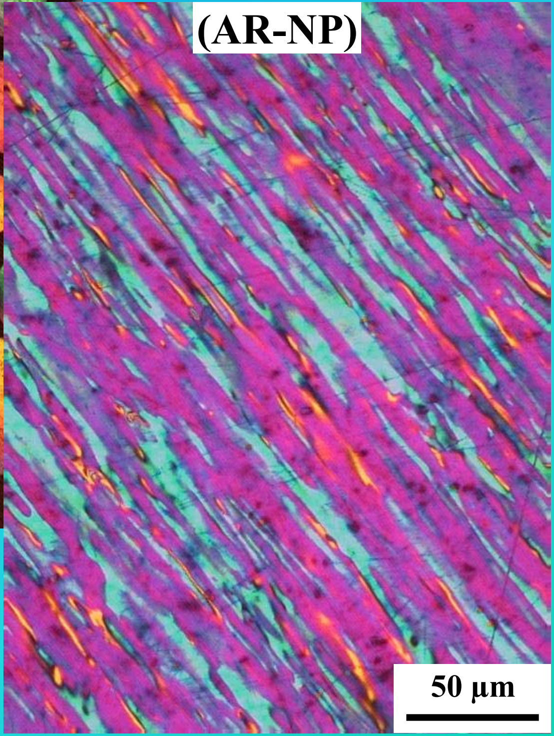
Pitch carbonization



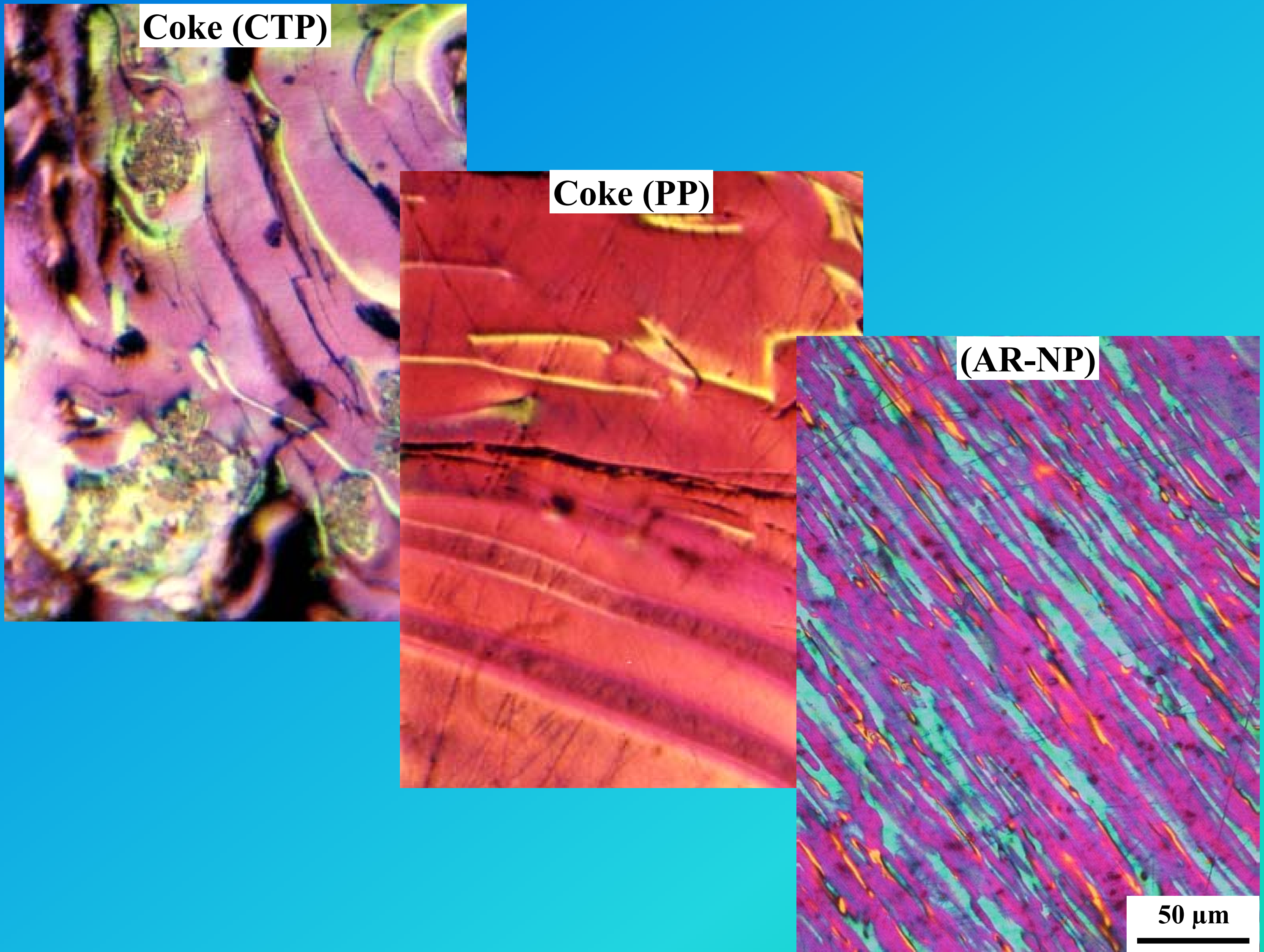
Pitch carbonization. Mesophase







Pitch carbonization. Coke

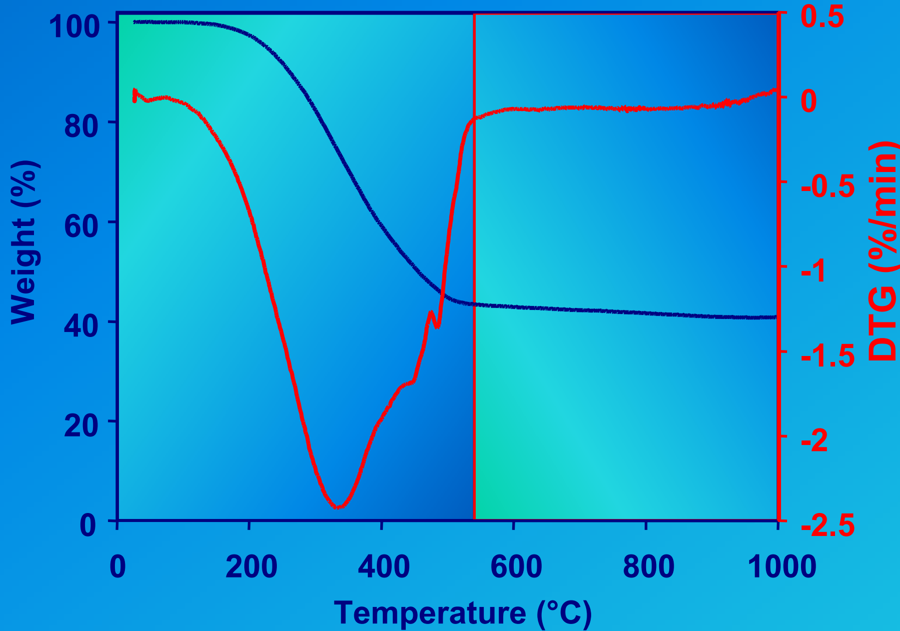


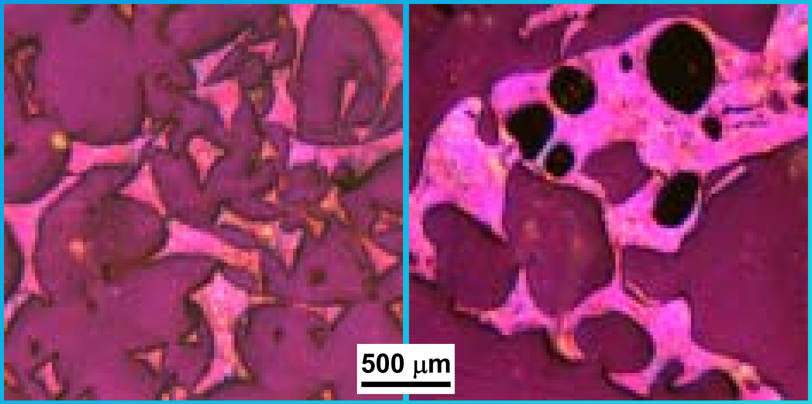
Pitch as a Precursor for Advanced Carbon Materials

<u>ADVANTAGES</u>

- Highly aromatic (graphitizability)
- Adequate viscosity
- High carbon yield
- Good adhesion (carbon particles)
- Highly available
- Low cost

Industrial Pitch as a Carbon Precursor





- Swelling
- Brittleness
- Porosity

Industrial Pitch as a Carbon Precursor - II

COMERCIAL PITCH

ADVANCED USES

- Carbon fibres
- Carbon composites

TREATED PITCH

Modification of Pitches

Why pitch should be modified? How pitch can be modified?

- ⇨To reduce porosity
- ⇨To increase carbon yield
- ⇨To design a carbon precursor with specific properties

⇧

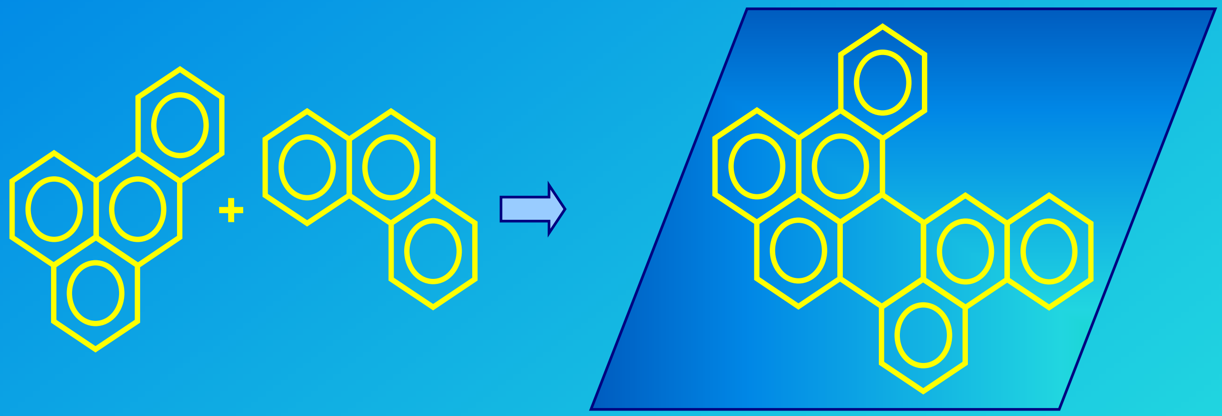
Pitch modification

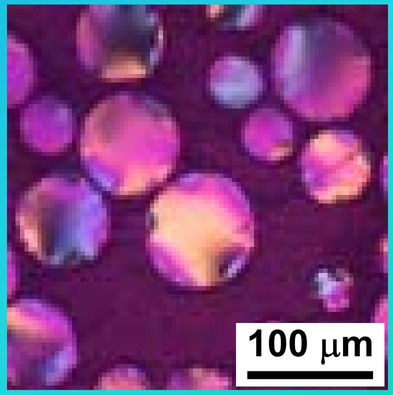
⇩

- ⇨THERMAL TREATMENT IN AN INERT ATMOSPHERE
- ⇨THERMAL TREATMENT IN THE PRESENCE OF AIR (air-blowing)

Thermal treatment of pitches

- Interrupted carbonization (350-450 °C)
- Inert atmosphere (N_2)
- Distillation
- Polymerization (planar macromolecules)



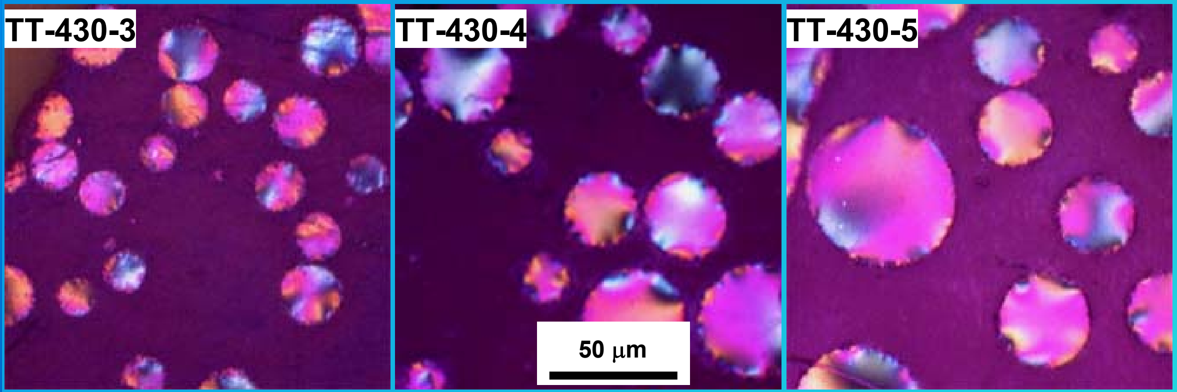


Thermal treatment of pitches - II

Pitch	Treatment	C/H	SP	TI	NMPI	CY	M	∅
A0	None	1.68	95	21.3	4.9	49.0	0.0	-
A1	420 °C / 6 h	2.01	178	55.2	36.7	72.8	30.0	10-30
A2	420 °C / 7 h	2.06	202	60.7	40.5	77.3	39.4	10-40
A3	420 °C / 8 h	2.08	222	63.8	43.1	78.8	41.6	20-40

C/H, carbon/hydrogen atomic ratio
SP, softening point (Mettler, °C)
TI, toluene-insoluble content (wt.%)
NMPI, N-methyl-2-pyrrolidinone-insoluble content (wt.%)

CY, carbon yield (Alcan, wt.%)
M, mesophase content (vol.%)
∅, sphere mean diameter (μm)



- ➢Dehydrogenative polymerizatio
- ➢Increasing in SP
- ➢Increasing in TI and NMPI
- ➢Increasing in CY
- ➢Mesophase formation
- ➢Spheres of larger size

Separation of phases in TT pitches. Motivations

PITCH

THERMALLY TREATED PITCH
(Isotropic phase + Mesophase)

ISOTROPIC PHASE

MESOPHASE

✓SCIENTIFIC: To study the partial contribution of each phase to the whole pitch

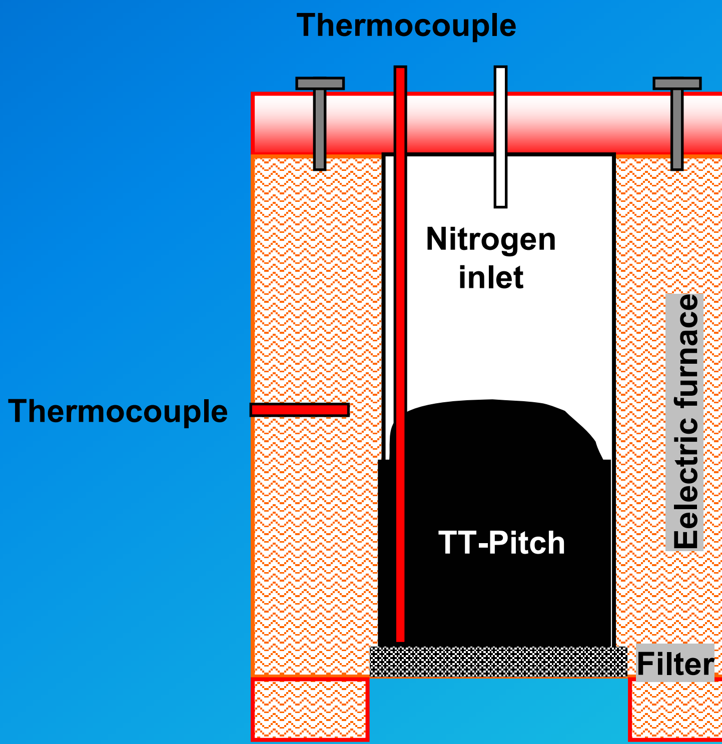
✓TECNOLOGIC: To obtain new precursors for carbon materials, especially mesophase

<u>MESOPHASE ISOLATION</u>

✓Filtration

✓Sedimentation

Separation of phases in TT pitches. Procedure



- ⇨ Stainless steal reactor
- ⇨ 300-350 °C
- ⇨ 0.5 MPa N_2
- ⇨ Filter 5 μm mesh
- ⇨ 500 g pitch

COAL-TAR PITCH

HOT FILTRATION UNDER PRESSURE

- ⇨ Phases with different softening point
- ⇨ Filtrated consisting of 100 % isotropic phase
- ⇨ Filtration residue enriched in mesophase (85-95 vol.%)
- ⇨ No coalescence of the mesophase
- ⇨ Phases are not altered

Separation of phases in TT pitches. Characteristics

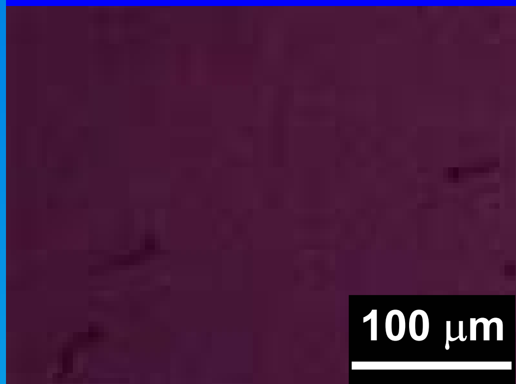
Pitch	M	C/H	SP	TI	NMPI	CY
TT430-3	25	1.89	174	53.9	29.8	61.5
Isotropic Phase	0	1.85	169	45.8	16.3	56.2
MESOPHASE	80	2.05	-	66.7	53.4	74.9

M, mesophase content (vol.%)
C/H, carbon/hydrogen atomic ratio
SP, softening point (Mettler, °C)
TI, toluene-insoluble content (wt.%)
NMPI, N-methyl-2-pyrrolidinone-insoluble content (wt.%)
CY, carbon yield (900 °C, wt.%)

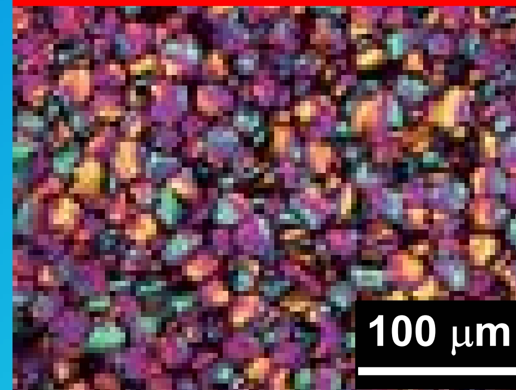
- ⇨ **Mesophase is more polymerized than the isotropic phase**
- ⇨ **Treated pitch a combination of the two phases**

Separation of phases in TT pitches. Applications

ISOTROPIC PHASE



MESOPHASE



ISOTROPIC PHASE

O.T. coke highly orientated

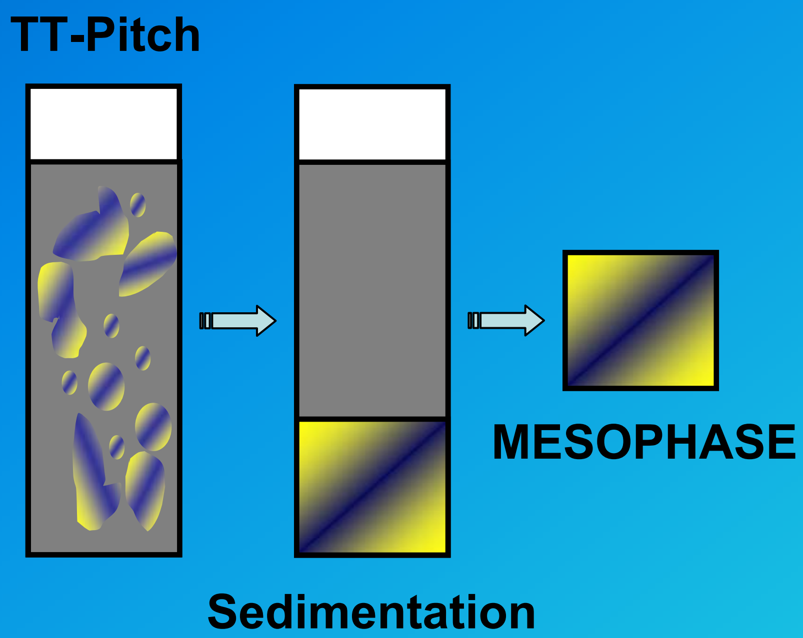
CARBON FIBRES

MESOPHASE

Homogeneous-size spheres

POLYGRANULAR GRAPHITES

Mesophase isolation. Sedimentation



QI-FREE PITCHES (PP)

HOT SEDIMENTATION

- ⇨400-450 °C (~420 °C , 1h)
- ⇨Phases with different density
- ⇨Bottom phase almost 100 % mesophase
- ⇨Phases are not altered

Mesophase properties and applications

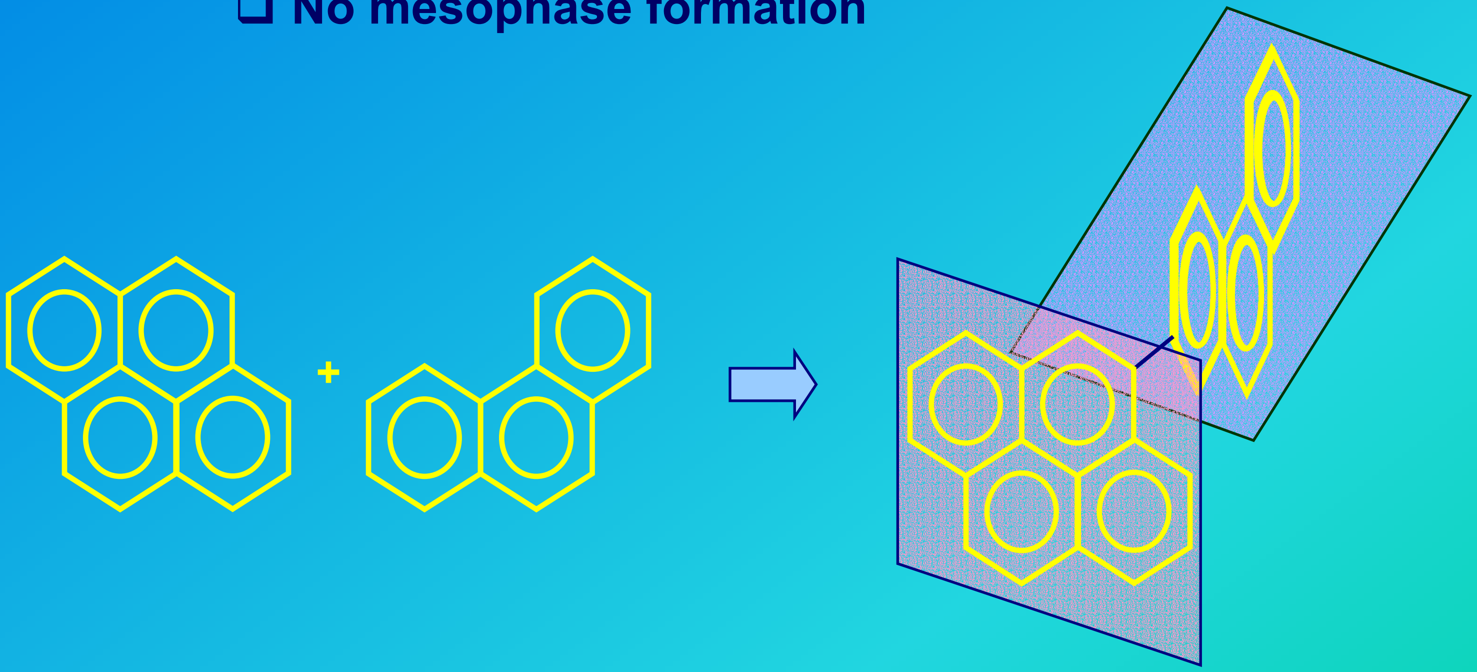
Pitch	M	C/H	SP	TI	NMPI	CY
PP	0	1.52	127	3.6	0.3	-
TT-PP	28	1.95	210	52.9	27.0	78.5
MESOPHASE	96	2.14	317	76.5	61.4	86.1

M, mesophase content (vol.%)
C/H, carbon/hydrogen atomic ratio
SP, softening point (Mettler, °C)
TI, toluene-insoluble content (wt.%)
NMPI, N-methyl-2-pyrrolidinone-insoluble content (wt.%)
CY, carbon yield (900 °C, wt.%)

MESOPHASE → **CARBON FIBRES**

Oxidative treatment of Pitches

- Temperatures < 350 °C
- Reaction times 10 h
- In the presence of air (oxygen)
- Distillation
- Planar macromolecules
- Cross-linked olygomers
- No mesophase formation



Oxidative treatment of Pitches - II

Pitch	Treatment	O	C/H	SP	TI	NMPI	CY
B0	None	1.80	1.64	97	20.0	4.7	34.6
B1	275 °C / 10 h	1.78	1.72	139	36.6	13.6	48.0
B2	275 °C / 18 h	1.81	1.83	168	44.6	18.1	57.6
B3	275 °C / 25 h	1.89	1.86	197	51.8	24.9	61.8
B4	275 °C / 30 h	1.86	1.87	210	52.0	27.1	62.7

O, oxygen content (wt.%)
C/H, carbon/hydrogen atomic ratio
SP, softening point (Mettler, °C)
TI, toluene-insoluble content (wt.%)
NMPI, N-methyl-2-pyrrolidinone-insoluble content (wt.%)
CY, carbon yield (900 °C, wt.%)

- Dehydrogenative polymerization
- No oxygen uptake
- Increase in softening point
- Increase in insoluble content
- Increase in carbon yield

New Tendencies in Pitches

New tendencies in pitches

POLLUTION AND WORKERS HEALTH (non-controlled environments)

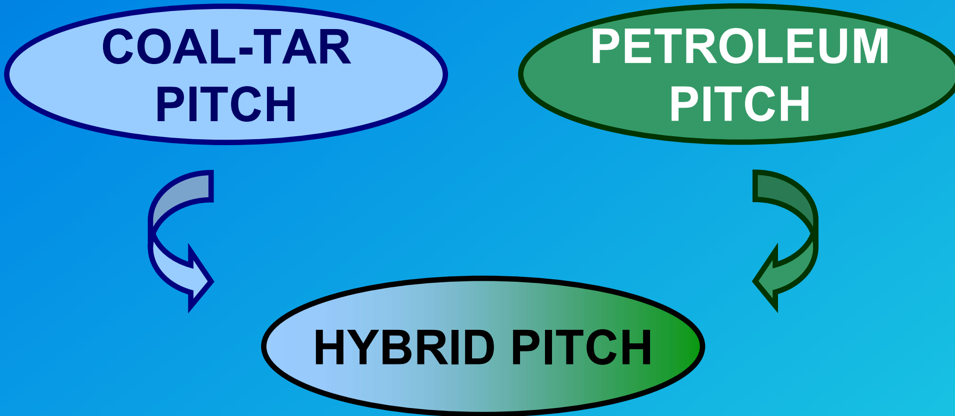
⇨ Emission of toxic and/or carcinogenic PAHs to the atmosphere and the working space

Coal tar

COAL TAR SUPPLY AND LOCATION

⇨ Reduction in coal tar production in the West Europe countries and coal tar produced far away from coal tar distillers

CTP+PP hybrid pitches



<u>COAL-TAR PITCH</u>

- ❑ Inherent binder capacity
- ❑ Appropriate viscosity and wetting behaviour

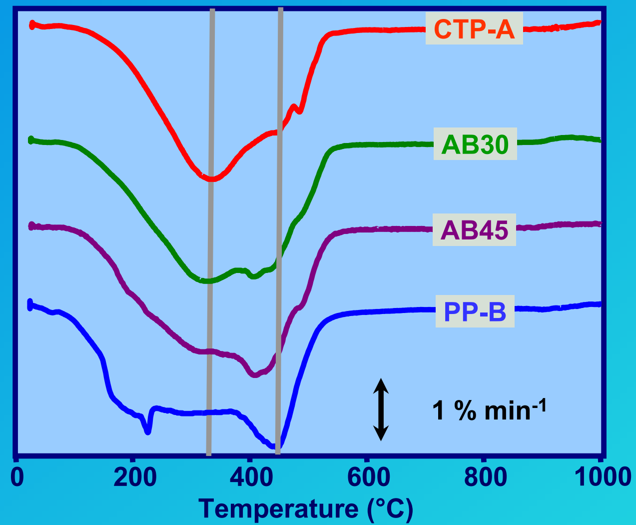
<u>PETROLEUM PITCH</u>

- ❑ Lower content in metals
- ❑ Lower content in genotoxic PAHs

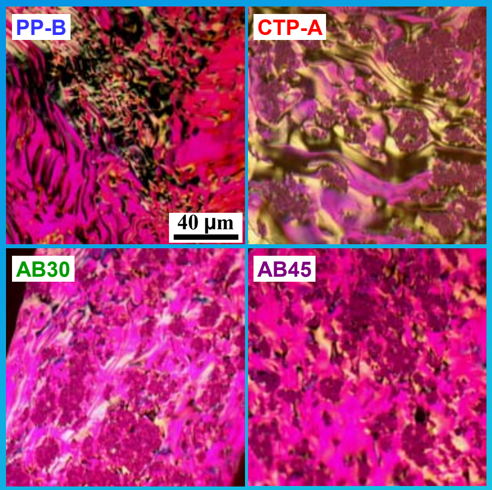
CTP+PP hybrid pitches - II

CTP-A/PP-B (70:30)	→	AB30
CTP-A/PP-B (55:45)	→	AB45

PR =
M =
IQ ↓



COKES (900 °C)



	CTP-A	AB30	AB45	PP-B
Benzo[a]Pyrene (ppm)	8,276	4,958	3,297	904

Lab carbon anodes (Söderberg) with similar properties

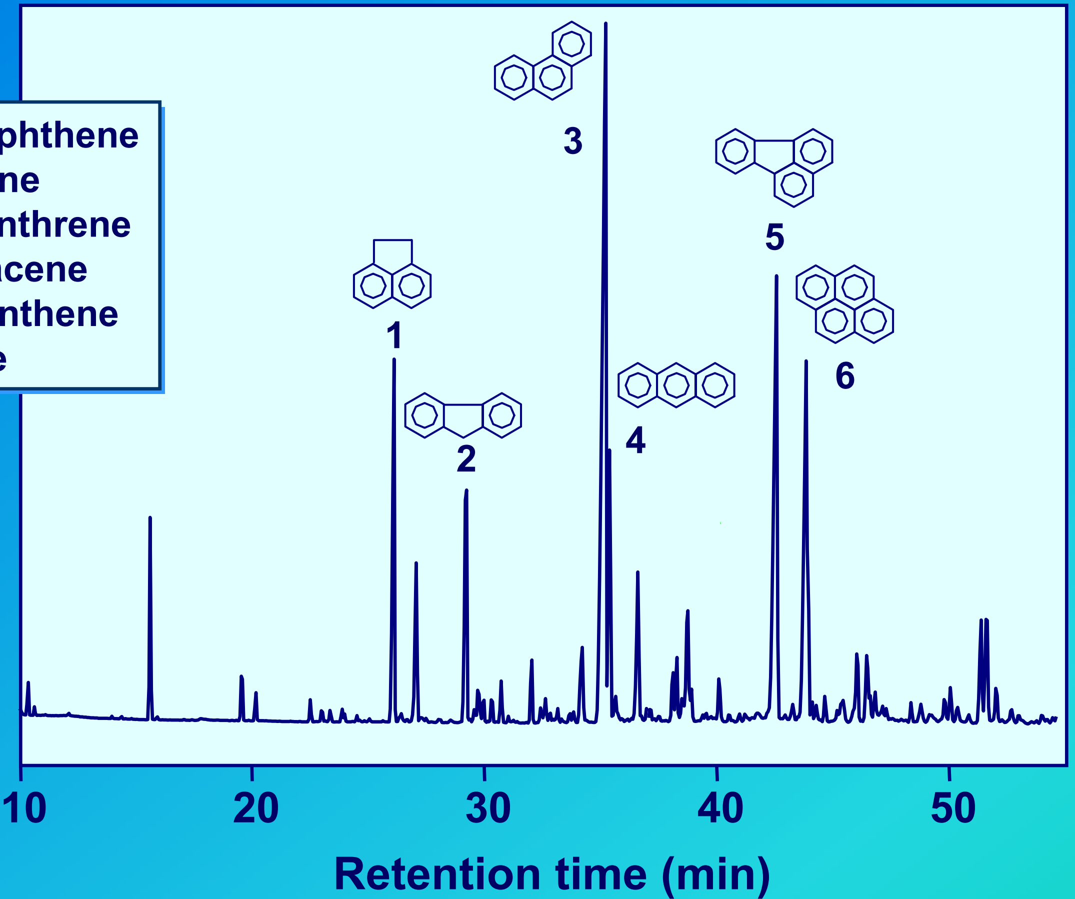
Anthracene oil-based pitches

Why?

- **Anthracene oil is highly aromatic**
- **Representative coal-tar fraction, in terms of percentage (30%)**
- **Low value product**
- **It is a heavy coal-tar distillation fraction susceptible to be transformed into pitch**
- **Uniform composition**
- **Possibility to produce a semi-synthetic pitch**
- **…..**

Anthracene oil-based pitches - II

1.Acenaphthene
2.Fluorene
3.Phenanthrene
4.Anthracene
5.Fluoranthene
6.Pyrene



- Anthracene oil mainly consists of 3-5 ring PAH
- Components stable at their boiling point
- Condensation cannot be performed by thermal treatment at atmospheric pressure

Anthracene oil-based pitches - III

Oxidative
Aromatic Condensation

Thermal & Chemical
Treatment

Distillation
90-110 ºC, Mettler SP

•250-295 °C

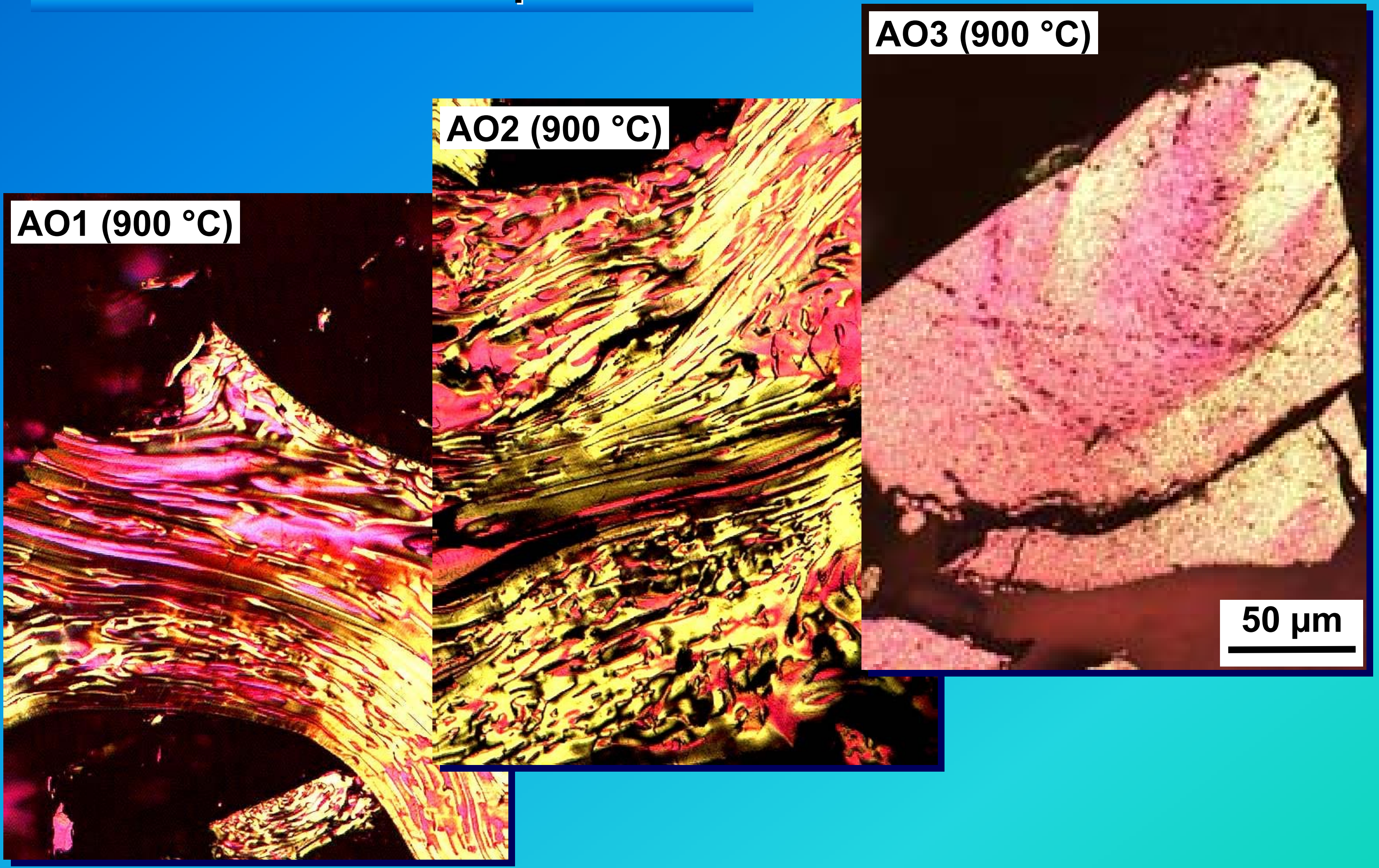
Anthracene oil-based pitches - IV

Pitch	SP	QI	β-R	S	CY	B[a]P
B-CTP	110	10.0	18-20	< 0.6	53	10.8
110-AOP	110-115	0.3-1.0	23-28	< 0.6	45-47	1.7-14.0
I-CTP	90	1.3	15-16	< 0.6	41	12.8
90-AOP	90	0.3-0.5	20-23	< 0.6	39-41	3.4-14.0

SP, Mettler softening point (°C)
QI, quinoline insolubles (wt.%)
β-R, beta resin content (wt.%)
S, sulphur content (wt.%)
CY, Sers carbon yield (wt.%)
B[a]P, Benzo[a] pyrene content (mg/g)

	CTP	AOP
Wetting (°C)	135	135-137
Filtration rate (g)	18 (80 min)	60 (40-50 min)

Anthracene oil-based pitches - V



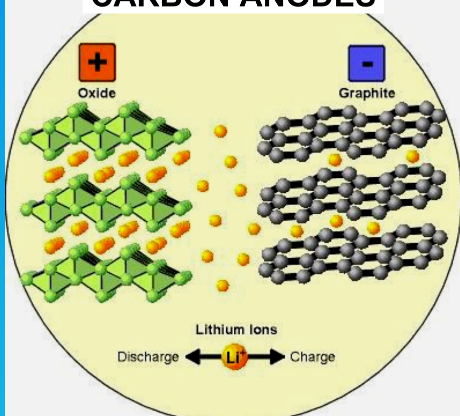
Severity of the oxidative treatment

Anthracene oil-based pitches - VI

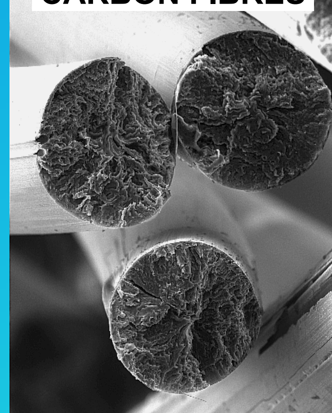
ANTHRACENE OIL BASED PITCHES

- Uniformity in pitch composition
- High fluidity
- Highly aromatic composition
- Semi-synthetic pitches
- Absence of solid particles & metals
- High flexibility to produce carbons with different O.T.

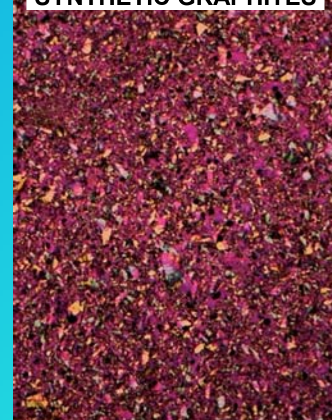
CARBON ANODES



CARBON FIBRES



SYNTHETIC GRAPHITES



CARBON PREFORMS (Impregnation)

Concluding remarks

•The main application of coal-tar pitch is as binder and impregnating agent in industrial processes (aluminium and graphite technology).

•Coal-tar pitches can be used as advanced carbon precursors.

•Recent development in pitch production allows pitches from heavy tar distilled fractions (i.e., anthracene oil) to be obtained. AOPs represent a new generation of pitches with specific properties, and consequently, other potential applications which have still not been studied.

R&D Projects

Regional Government

- Development of high-performance carbon materials from anthracene oil-based precursors (2004-2006)
- **Development of carbon-based supercapacitors for high power electronic applications (2005-2007)**

R&D Projects

National Programmes

- Preparation of new binders from petroleum residues for their use in the fabrication of electrodes (1999-2001)
- Preparation of carbon fibres and synthetic graphites from coal-tar pitches (2000-2001)
- Optimization of pitch/graphite/copper systems for electrical applications (2000-2003)
- New carbon anodes for ion-lithium batteries (2001-2004)
- Development of new petroleum pitches for magnesia-carbon composites (2003-2007)
- **Development of nanoporous carbon materials for carbon storage (2004-2007)**
- **Reduction of carcinogenic emissions in the production of carbon anodes by means of petroleum pitches (2005-2007)**
- **Carbon materials for lithium ion batteries anodes (2007-2009)**

R&D Projects

European Programmes

- New materials for extreme environments (2004-2008)
- Development of a new generation of coal-derived environmentally-friendly pitches (2005-2008)